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One dimensional molecular dynamics simulations of the onset of detonation have been performed using three-body potentials which accurately reproduce the effects of endothermic bond breaking and exothermic bond recombinations. A stable detonation wave of reasonable velocity can be produced from the impact of a plate upon a stationary array of diatomic molecules. The onset of detonation has been studied using a variety of potential forms including LEPS and Tersoff potentials. Properties of the detonation front, including from velocity, reaction zone width, and product distribution, have been studied as functions of barrier height, exothermicity, and other relevant potential function parameters. A model is proposed to explain the self-regulating detonation front velocities observed in these simulations in terms of atomic-scale kinetics.

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SOME ONE-DIMENSIONAL MOLECULAR DYNAMICS SIMULATIONS OF DETONATION*

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SOME ONE-DIMENSIONAL MOLECULAR DYNAMICS SIMULATIONS OF DETONATION

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One-dimensional molecular dynamics simulations of the onset of detonation have been performed using three-body potentials which accurately reproduce the effects of endothermic bond breaking and exothermic bond recombinations. A stable detonation wave of reasonable velocity can be produced from the impact of a plate upon a stationary array of diatomic molecules. The onset of detonation has been studied using a variety of potential forms including LEPS and Tersoff potentials. Properties of the detonation front, including front velocity, reaction zone width, and product distribution, have been studied as functions of barrier height, exothermicity, and other relevant potential function parameters. A model is proposed to explain the self-regulating detonation front velocities observed in these simulations in terms of atomic-scale kinetics.

1. INTRODUCTION

The study of the onset of detonation at the molecular level is a difficult experimental task because of the short time scales involved and the destructive nature of the detonation process. Computer simulations are an obvious alternative, but the continuum methods which are so valuable for predictions at the macroscopic level are unable to give information regarding the primary chemical processes occurring in the reacting solid. Molecular dynamics simulations, on the other hand, are feasible under precisely the conditions of interest: short times and relatively small numbers of molecules. Indeed, molecular dynamics simulations of *nonreactive* shock waves have been performed for more than two decades. For the study of detonation, however, the simulations must explicitly include the chemical reactions which provide the energy to sustain the process. This requires the use of many-body potential functions which correctly reproduce the salient features of detonation reactions, but yet are simple enough to make the simulation computationally feasible.

We report two types of many-body potential functions which are capable of accurately describing bond-breaking and bond-forming behavior in simple model systems of detonating solids. We demonstrate that one-dimensional molecular dynamics simulations using these potentials produce self-sustaining detonation waves with stable velocities independent of initiation conditions. Finally, we offer a molecular interpretation for the stability of the detonation velocities.

2. THE LEPS POTENTIAL

One form of potential function which can give qualitatively correct bond-breaking and bond-forming behavior for simple systems is the LEPS (London, Eyring, Polanyi, Sato) potential, developed in the 1930's to describe the H_3 potential energy surface. In the form devised by Tully[1], a three-body LEPS potential function can be described in terms of 2x2 matrices as follows: For each pair of atoms ij in the three-body system, a diagonal 2x2 matrix is constructed in which $H_{11} = V_{bond}(r_{ij})$ and $H_{22} = V_{nonbond}(r_{ij})$, where r_{ij} is the scalar distance between atoms i and j, V_{bond} is a typical diatomic bonding potential such

as a Morse function, and V_{vdw} is a weak van der Waals attraction between atoms i and j. The total potential energy of the three-body system, assuming nearest-neighbor interactions only, is then given as the lower eigenvalue of the 2x2 hamiltonian

$$H = H_0 + \ldots R$$

where R is the rotation matrix corresponding to a 60° two-dimensional rotation.

The LEPS potential is particularly suitable for one-dimensional simulations because in such systems each atom has exactly two nearest neighbors and therefore forms the central atom of a three-body system. The total potential energy of a one-dimensional crystal can be expressed as a sum of overlapping LEPS three-body potentials in which each atom (except those on the ends) appears as a left-hand, central, and right-hand member of three different trimers. The potential energy and atomic forces can be expressed analytically, so the method is computationally efficient.

We have recently reported[2] preliminary results of some one-dimensional molecular dynamics simulations using LEPS potentials designed to represent the features of detonating nitric oxide system, 2NO → N2 + O2. The initial NO crystal is arranged in the form ··· NO ON NO ON ··· so that formation of the appropriate products is possible. The NNO and NOO LEPS potentials are parameterized to match experimental exothermicities and calculated barrier heights for the three-body reactions N + NO → N2 + O and N + O2 → NO + O. The detonation is initiated by impact of a small nitric oxide plate upon one end of the larger crystal. The simulation can readily be followed over the course of 20 picoseconds, during which time the detonation front propagates through several thousand atoms.

The most striking feature of these simulations is that the detonation velocity is independent of the plate impact velocity, as long as the impact is strong enough to cause bond ruptures which initiate the detonation reactions. If the plate impact velocity is too great the detonation is initially overdriven, but quickly returns to its steady-state value. If the impact velocity is too low to initiate detonation, it causes a gradually decaying nonreactive shock wave to propagate through the system. The lack of dependence of the detonation velocity on initiation conditions is in agreement with experimental observations of condensed-phase detonation.

Figure 1 shows the atomic density relative to the front for a plate impact speed of 6 km/sec, averaged over the course of a 20 picosecond simulation. Most of the chemical reactions take place in the high-density region within 400 Ångstroms of the front; behind this region the density falls off rapidly as the products and unreacted fragments separate. Further reaction in this gas-phase-like region is less likely because of the larger average interatomic spacing and small relative velocities which prevail in this region.
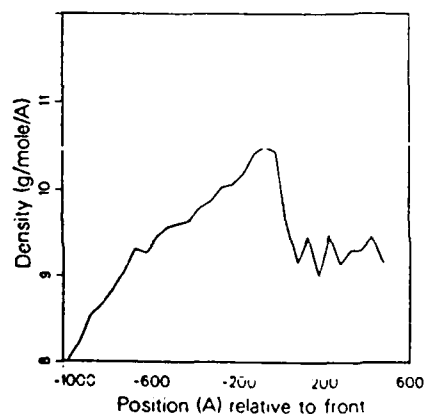

FIGURE 1
Density (g/mole/Å) versus position relative to the front for a plate impact speed of 6 km/sec.

3. THE TERSOFF POTENTIAL

One difficulty with the LEPS potential is the lack of a straightforward scheme for extending the method to higher dimensions with arbitrary numbers of near neighbors. We have therefore investigated the use of another form of empirical reactive potential based on the work of Tersoff. The Tersoff method uses a modified pair potential in which the bonding part of the interaction between a pair of atoms i and j is weakened by an amount proportional to the number of other near neighbors which compete for bonding to atom i, i.e.,

$$E = \sum_i E_i$$

where

$$E_i = (1/2)\sum_{j \neq i} (V_R(r_{ij}) - B_{ij} \cdot V_A(r_{ij}))$$

Here V_R represents a repulsive potential, V_A is an attractive potential, and B_{ij} represents a many-body coupling between bond ij the local coordination of atom i. These three functions can be implemented in a variety of ways[4,5], giving the Tersoff potential a great deal of flexibility. In particular, the coupling term B_{ij} may depend on the angle of a competing bond ik to the bond ij, thereby incorporating directed valence effects of importance for covalent compounds in two and three dimensions.

We have constructed a one-dimensional Tersoff potential to represent the generic reaction 2AB → A_2 + B_2, where the AB molecules have been given a bond strength of 4 eV and the A_2 and B_2 molecules have each been assigned a bond energy of 5 eV so that the overall reaction is exothermic. An initial AB molecular crystal was constructed in a manner identical to the nitric oxide simulations described above, ··· AB BA AB ···, and the stability of the reactant solid was ensured by incorporating barrier heights of 0.5 eV for the two possible three-body reactions A + AB → A_2 + B and B + BA → B_2 + A (which are energetically equivalent in this case) and weak long-range van der Waals attractions between AB

molecules. Details of the potential function will be presented elsewhere.

As in the nitric oxide LEPS simulations described above, molecular dynamics simulations of the detonation of this system were carried out, with the detonation initiated by impact of a mass of variable velocity on the reactant solid. Although the density, exothermicity, and the potential surfaces in this case were quite different from those employed in the nitric oxide simulations, the results were qualitatively similar. For impact velocities ranging from 4 km/sec to 9 km/sec, the detonation velocity rapidly stabilized to a constant value of 12.6 km/sec. Exothermic chemical reactions in a high-density region behind the front provided the energy to sustain the detonation. Impact velocities less than 4 km/sec or greater than 9 km/sec did not produce detonation; in these cases the disturbance propagated through the chain as a gradually dissipating nonreactive shock wave.

4. VELOCITY REGULATION MECHANISM

The self-limiting detonation velocity observed in the simulations can be understood by investigating the behavior of an isolated three-body reaction process, A + AB → A_2 + B. Classical trajectory calculations on the Tersoff potential surface described above lead to the results shown in Figure 2, where the velocity of product atom B is plotted as a function of the velocity given to an incident reactant atom A. The straight line marks the condition that the velocity of the outgoing atom equals the velocity of the incoming atom. The lower value of the curve is determined by the smallest velocity of atom A, which can overcome the potential barrier to reaction. The upper value of the curve represents the point beyond which the impact of atom A leads only to endothermic fragmentation (A + A + B) or to no reaction (A + AB).

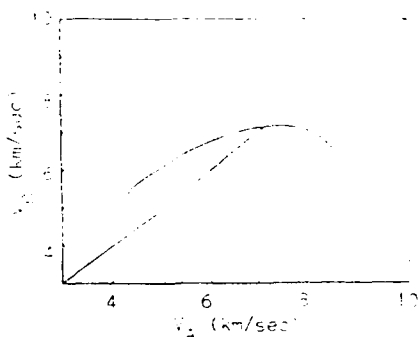If detonation in one dimension is viewed as being driven by a series of three-body reactions

FIGURE 2
Outgoing velocity of atom B following the reaction
A + AB → A$_2$ + B, as a function of the velocity of
the incoming atom A relative to a stationary AB
molecule. The straight line indicates equal
incoming and outgoing velocities.

in which the products of one reaction collide with
a molecule to initiate a new reaction, then the
detonation regime will be limited to the range of
impact velocities which cause initiation of the
exothermic reactions A + AB → A$_2$ + B and B + BA →
B$_2$ + A. This analysis should also be valid in
higher dimensions, as cross sections for bond
dissociation generally increase for increasing
atomic collision energies.

For incoming velocities near the low end of
the reaction range, the velocity of the product
atom is greater than that of the reactant atom.
This is due to the net exothermicity of the
reaction, and has the effect of accelerating the
atomic velocities. For higher incident
velocities, however, the outgoing atom has a lower
velocity than the incoming atom. This occurs
because the trajectory interacts with the
repulsive wall of the potential surface,
increasing the amount of energy deposited in the
internal vibrational mode of the product molecule
A$_2$. If a series of isolated reactions in the
orientation present in the chain described above
are initiated with an atom anywhere within the
range of reacting velocities, the series will
"self regulate" to the point at which the two
curves cross in Figure 2. Of course, in the solid

...... the detonation velocity will
significantly higher than the above analy..
predicts, because the detonation wave i. .
collective disturbance which can propagate faster
than individual atomic velocities. This effect
can be accounted for quantitatively by includir:
in the analysis the effect of the density of th
chain, or more accurately the fraction of the unit
cell length excluded by repulsive atomic core
potentials.

5. CONCLUSION

Molecular dynamics simulations of detonation
can be carried out in one dimension with many-body
potential functions which incorporate realistic
reaction dynamics. These simulations can provide
valuable insight into the chemical mechanisms
underlying the initiation and propagation of
detonation. The Tersoff potential is particularly
well suited to the extension of these
investigations to two and three dimensions.

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